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(19) (CA) **CANADIAN PATENT** (12)

(54) REGENERATION OF SPENT SO<sub>2</sub>-SO<sub>3</sub> SORBENTS  
WITH H<sub>2</sub>S AT MODERATE TEMPERATURE

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No. OF CLAIMS 6 - NO DRAWING



BRIEF DISCLOSURE

10        The metal oxides  $\text{CeO}_2$ , either supported or unsupported,  
used to remove sulfur oxides from waste gas effluent streams by  
conversion into cerium sulfate and/or cerium oxysulfate, is re-  
generated to the starting cerium oxide by means of a reducing  
regenerating atmosphere consisting essentially of  $\text{H}_2\text{S}$  as the re-  
ducing component at a concentration of from 0.5 to 100 vol. %,  
preferably 1-70 vol. %, most preferably 5-70 vol. %, the balance  
comprising non-regenerating non-reactive and inert gases such as  
helium, argon,  $\text{CO}_2$ , nitrogen, water vapor, etc. at a temperature  
of from 300-700°C, preferably 350-700°C, most preferably 450-600°C  
in the presence of sufficient oxygen to convert any  $\text{SO}_2$  in said  
gas to  $\text{SO}_3$ , (in the  $\text{SO}_2$  removal step) the reducing-regenerating  
atmosphere passing at any convenient rate, such as from 50 to  
50,000 V/V/Hr, preferably 100 to 50,000 V/V/Hr, most preferably  
100-20,000 V/V/Hr.

20        Regeneration is typically conducted on the cerium oxide  
sorbent which has been converted to cerium sulfate, and/or oxy-  
sulfate to the extent of 10 to 100 mole %, preferably 10-70 mole %.  
Regeneration of the cerium-sulfur oxide compounds to the cerium  
oxide is accompanied by the liberation of  $\text{SO}_2$  which is conveniently  
used with additional  $\text{H}_2\text{S}$  in a Claus plant for conversion to ele-  
mental sulfur.

DISCLOSURE

Metal oxides selected from the group consisting of  $\text{CeO}_2$ ,  
copper oxides, iron oxides, preferably  $\text{CeO}_2$ , either supported or  
unsupported, which have been used as a sorbent to scrub sulfur  
oxides (i.e.  $\text{SO}_2$ ,  $\text{SO}_3$ , etc.) from waste gas effluent streams and are



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th reby conver' d to the metal sulfate, and/or metal oxysulfate  
(for use of  $\text{CeO}_2$  see U.S. Patent 4,001,375).



are regenerated to the metal oxide by means of a reducing regenerating atmosphere consisting essentially of  $H_2S$  as the reducing-regenerating component present at from 0.5 to 100 vol. %, most preferably 5 - 70 vol. %, the balance comprising nonregenerating inert gases such as helium, neon, argon,  $CO_2$ , nitrogen, water vapor, etc. and mixtures thereof, at a temperature from 300-700°C, preferably 350-700°C, most preferably 450-600°C, the reducing-regenerating atmosphere stream passing through the sorbent at any convenient rate, such as from 50 to 50,000 V/V/Hr, preferably 100 to 50,000 V/V/Hr., most preferably 100 to 20,000 V/V/Hr. This regeneration procedure can be practiced on either a cyclic or continuous basis.

The regeneration procedure of the instant invention is utilized in flue gas desulfurization processes in which the flue gas is contacted with a sorbent comprising cerium oxide in either the +3 or the +4 oxidation state. Preferably, the cerium oxide is supported on an inert support. The support is preferably an inorganic refractory oxide, for example, various aluminas, silica, etc. The support can be of various shapes, such as pellets, extrudates, Raschig rings, saddles or monoliths, e.g. honeycombs. The most preferred support is  $\gamma$ -alumina, especially in the shape of Raschig rings.

The support will have a surface area of from 10 m<sup>2</sup>/g to 300 m<sup>2</sup>/g, preferably from 100 m<sup>2</sup>/g to 200 m<sup>2</sup>/g. The cerium oxide is combined with the support at from 1 to 40 wt. % of said support. Preferably, the sorbent will comprise from 2 to 20 wt. % cerium oxide.





In the following discussion  $\text{CeO}_2$  will be used as the specific example, it being understood that equivalent arguments and descriptions are available and operable for other

metal oxide sorbents unless specifically indicated otherwise. The supported cerium oxide sorbent may be prepared by methods known in the art for preparing supported catalysts for use in petroleum processes, e.g. reforming, hydrocracking, etc. For example, an aqueous solution of a cerium oxide precursor may be impregnated onto an alumina support. The impregnated support may be subsequently separated from excess solution, dried at a temperature of from about  $20^\circ$  to  $110^\circ\text{C}$  and calcined at a temperature of from about  $300^\circ\text{C}$  to  $600^\circ\text{C}$ . During the drying and/or the calcining step, the supported catalyst may be contacted with air or  $\text{O}_2$  to convert the cerium oxide precursor compound on the support into the oxide.

An alternative approach to the preparation of a cerium oxide impregnated support which places the  $\text{CeO}_2$  on the outer surface of a porous support involves prefilling of the pores with an inert liquid as described in U.S. Patent 2,746,936,

For convenience, the catalyst is impregnated with an aqueous solution of the cerium oxide precursor. However, organic solvents may be utilized provided the cerium oxide precursor is soluble therein. Precursors of the preferred sorbent, cerium oxide, which are soluble in aqueous solutions, include ceric ammonium nitrate, cerous nitrate, basic ceric nitrate, cerous acetate, etc. For other metal oxides, similar metal salts may be utilized.

The waste gas effluent stream scrubbed is typically a

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1 gas, preferably a flue gas, which comprises from 0.01 to 2.0%  
2 by volume (100 ppm to 20,000 ppm) sulfur oxides. This waste  
3 gas stream is contacted with the sorbent described above.  
4 Additionally, the waste gas stream contains  $O_2$  sufficient to  
5 convert all  $SO_2$  to  $SO_3$  and may also comprise  $N_2$ ,  $CO_2$ ,  $CO$ ,  $H_2O$ ,  
6  $NO_x$ , etc. It should be noted that none of these additional  
7 components will interfere with the scrubbing of the gas stream.  
8 In practice, at least a stoichiometric quantity of oxygen in the  
9 waste gas is needed to permit the absorption of  $SO_2$  on  $CeO_2$   
10 to form the sulfate or oxysulfate. During the initial contacting  
11 step, the temperature is maintained at from  $300^\circ C$  to  $700^\circ C$ ,  
12 most preferably from  $450^\circ C$  to  $600^\circ C$ . The pressure is not  
13 critical. For convenience, whatever pressure is obtained at  
14 the flow and temperatures utilized will be acceptable. The  
15 flow of the flue gas through the initial contacting zone, i.e.  
16 the zone in which the sorbent is contained, may vary from 50  
17 to 50,000, preferably from 500 to 50,000, and most preferably  
18 from 500-20,000 V/V/Hr. In the initial contacting zone, the  
19 catalyst may be present in the form of pellets, extrudates,  
20 etc. After a certain time, depending on the above contacting  
21 conditions, the cerium oxide will be converted substantially  
22 to cerium sulfate and/or cerium oxysulfate.

23           When the conversion of the cerium  
24 oxide to the corresponding sulfate or oxysulfate reaches from 10-  
25 100%, preferably 10-70% of capacity, the sorbent is regenerated  
26 by the process of the instant invention utilizing an  $H_2S$  con-  
27 taining gas wherein the reducing-regenerating agent consists  
28 essentially of the  $H_2S$  present at a concentration of from 0.5  
29 to 100 vol. %, preferably, 1-70 vol. %, most preferably 5-



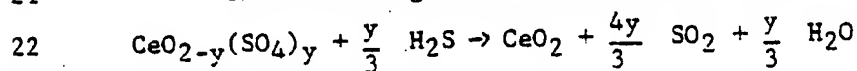
1 70 v l. %, the balance of the stream being nonregenerative,  
 2 nonreactive inert gas such as nitrogen, helium, argon, neon,  
 3 water vapor, CO<sub>2</sub>, etc. The cerium sulfate, and/or oxysulfate  
 4 is converted substantially to cerium oxide while the sulfur  
 5 is removed as sulfur dioxide from the sorbent.

6 When dealing with the cerium-system for example,  
 7 if reaction of the spent cerium sorbent with H<sub>2</sub>S goes too far  
 8 and begins to convert the regenerated cerium oxide to the  
 9 sulfide, a treatment with air, air/steam mixture, or steam  
 10 alone can be used to restore the sorbent to full capacity.  
 11 Preferably the atmosphere is steam. The temperature at which  
 12 this final step is performed (if it is necessary) ranges from  
 13 300-700°C, preferably, 400-700°C, most preferably 450 to 600°C.  
 14 This step converts any sulfide back to the oxide with only  
 15 small amounts of sulfate formation. The reaction of cerium  
 16 sulfide with oxygen to give almost quantitatively the oxide  
 17 is unique for cerium among the lanthanide sulfides which  
 18 generally burn to give oxysulfates.

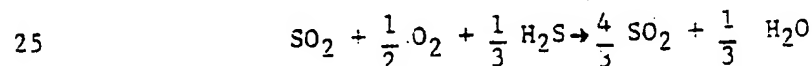
19 Cerium oxysulfates have the general formula:

20  $CeO_{2-y}(SO_4)_y$  where  $0 < y \leq 2$ .

21 The overall general regeneration reaction is:



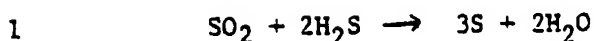
23 so that the overall method is to sequester SO<sub>2</sub> from a flue  
 24 gas and recover it as concentrated SO<sub>2</sub> as follows;



26 Any SO<sub>3</sub> present in the flue gas will also be removed.

27 The SO<sub>2</sub> thus formed can be reacted with additional  
 28 H<sub>2</sub>S over the amount needed to regenerate the sorbent to form  
 29 elemental sulfur by the Claus reaction:





2   which can be made to proceed in the same or a separate  
3   reactor from the  $\text{CaO}_2$  containing vessel. Note that a mole  
4   of  $\text{H}_2\text{S}$  is able to reduce three times as much sulfate as a  
5   mole of hydrogen, a major advantage of this method of regen-  
6   eration over the prior art.

7                   Alternatively, the  $\text{SO}_2$  thus formed may then be fed  
8   to a separate Claus plant for conversion to elemental sulfur.  
9   In the Claus plant  $\text{H}_2\text{S}$  is mixed with the  $\text{SO}_2$  to bring the  
10    $\text{H}_2\text{S}:\text{SO}_2$  mole ratio to 2:1 prior to the catalytic converter.

11                   One advantageous method of regenerating the spent  
12   metal oxide sorbent is to pass an excess of  $\text{H}_2\text{S}$ -containing  
13   gas over it, that is, in an amount in excess of the volume  
14   of  $\text{H}_2\text{S}$  needed to just regenerate the sorbent so that  $\text{H}_2\text{S}/\text{SO}_2$   
15   mixture is produced, which can be fed directly to the Claus  
16   plant. Indeed, some of the  $2\text{H}_2\text{S} + \text{SO}_2$  Claus reaction takes  
17   place over the metal oxide sorbent resulting in the production  
18   of some elemental sulfur in the sorbent vessel.

19                   As previously stated, this regeneration procedure  
20   can be practiced in either a cyclic or continuous manner.  
21   When operated in a cyclic manner the scrubber-regenerator  
22   comprises multibed units, wherein a gas mixture containing  
23   sulfur oxides is passed through one or more fixed beds of sup-  
24   ported cerium oxide. While these beds are scrubbing sulfur  
25   oxides, the other beds of the unit are being regenerated with  
26   an  $\text{H}_2\text{S}$  containing gas as described. The roles of the scrubber  
27   and regenerator are reversed when both have completed their  
28   task. Purging with a gas stream such as steam, between these  
29   two steps may be advantageous both to prevent explosive conditions





as well as for converting any cerium sulfide which may have formed in the regeneration step to cerium oxide.

In another embodiment of the instant invention, the catalyst is continuously removed and regenerated. For example, see the apparatus described in U.S. Patent No. 3,989,798.

As stated above, the cerium oxide is preferably supported on an inert support material to most economically use the cerium oxide. However, unsupported cerium oxide may be used provided adequate surface areas are obtained. Preferably the unsupported cerium oxide should have a surface area of at least 10 m<sup>2</sup>/g, preferably from 20 m<sup>2</sup>/g to 50 m<sup>2</sup>/g. Such unsupported cerium oxide is regenerated by the same H<sub>2</sub>S procedure as is supported cerium oxide.

#### EXAMPLES

A 5.5 g (8.2 cc) sample of 20% CeO<sub>2</sub> supported on extruded  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is held in place by quartz wool within a vertical quartz tube (~1" dia.). A gas blend containing 3700 ppm SO<sub>2</sub>, 5% O<sub>2</sub> and balance Ar is passed upward through the heated sample at 4000-5000 V/V/Hr. during the SO<sub>2</sub> scrubbing mode. The SO<sub>2</sub> content of the exit gas is analyzed using an electrochemical method containing a Faristor which is calibrated to read 100% at 5000 ppm SO<sub>2</sub>. During regeneration, a 1% H<sub>2</sub>S in He regeneration gas is run through the bed at ~1000 V/V/hr and the exit gas is bubbled through Pb(NO<sub>3</sub>)<sub>2</sub> solutions. A white precipitate (PbSO<sub>3</sub>) indicates SO<sub>2</sub> while a black precipitate (PbS) indicates H<sub>2</sub>S in the gas stream and signals the end of a regeneration.

A number of SO<sub>2</sub> scrubblings, H<sub>2</sub>S regenerations,



1 and optional burns were carried out under  
2 the conditions described above. Typically, during the SO<sub>2</sub>  
3 scrubbing, the SO<sub>2</sub> content in the exit gas as a function of  
4 time was as follows: 500 ppm/20 min; 1000 ppm/40 min; 1500 ppm/  
5 65 min; and 2000 ppm/95 min. The regeneration at 500-600°C with  
6 1% H<sub>2</sub>S He took about 1 hr. before breakthrough of H<sub>2</sub>S. The for-  
7 mation of cerium oxysulfate, oxide, and sulfide were all moni-  
8 tored by removing a small sample of extrudate at appropriate  
9 times and examining the product by X-ray diffraction.  
10 When a dry or wet H<sub>2</sub>S containing gas is used for the regen-  
11 eration, prolonged treatment of the spent sorbent may first  
12 convert it to the oxide, followed by further conversion to  
13 the sulfide, CeS<sub>2</sub>. It was also shown that the resultant sul-  
14 fide can be converted back to the oxide by passing an oxygen  
15 and/or steam containing gas over it at 300-700°C.

16 The present invention is particularly well suited  
17 for the removal of SO<sub>2</sub> from gases in an installation where  
18 stoichiometrically adequate amounts of H<sub>2</sub>S are also available  
19 from other operations. Typical examples are as follows:

- 20 (a) Claus plant tail gas cleanup.
- 21 (b) SO<sub>2</sub>/SO<sub>3</sub> removal from refinery flue gases.
- 22 (c) SO<sub>2</sub>/SO<sub>3</sub> removal from flue gases in coal gasi-  
23 fication or liquefaction plant, tar sand refineries, and the  
24 like where H<sub>2</sub>S is available as a byproduct.

" " "

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for desulfurizing an effluent waste gas stream comprising adsorbing sulfur oxides by a cerium oxide sorbent, at a temperature of from 300-700°C., in the presence of sufficient oxygen to convert any  $\text{SO}_2$  in said gas to  $\text{SO}_3$  and thereafter regenerating the spent cerium oxide sorbent, said process characterized in that said spent cerium oxide sorbent is regenerated by contacting said spent cerium oxide sorbent with an  $\text{H}_2\text{S}$  containing reducing-regenerating gas comprising from 0.5 to 100.0 volume percent  $\text{H}_2\text{S}$  with the balance comprising a non-regenerating gas, at a temperature of from 300-700°C. at a convenient flow rate.
2. The process of claim 1 wherein the  $\text{H}_2\text{S}$  containing reducing-regenerating gas flow rate ranges from 50 to 50,000 V/V/Hr.
3. A process according to claim 2 wherein the  $\text{H}_2\text{S}$  concentration in said reducing-regenerating gas ranges from about 1-70 volume percent.
4. A process according to claim 3 wherein said non-regenerating gas is helium,  $\text{CO}_2$ ,  $\text{N}_2$ , Ar, water vapor or mixtures thereof.
5. The process of claim 4 wherein said cerium oxide is exposed, as a final regeneration step, to steam, air or steam/air mixtures to convert any  $\text{CeS}_2$  to  $\text{CeO}_2$  and wherein said exposure is conducted at a temperature of from 300-700°C.



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6. A process according to any of one of claims 4 or 5 wherein said cerium oxide sorbent is supported on an inert support.

